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Characterization of nano-scaled calcium phosphate particles made using microwave assisted synthesis

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By instant microwave assisted synthesis, nanocrystalline hydroxyapatite was prepared that was rod-like shaped 42.3 ± 1.3 nm in length with a diameter of 15.3 ± 0.4 nm. The results from analysis such as thermogravimetric analysis, wide-angle X-ray diffraction, energy dispersive X-ray spectroscopy, and transmission electron microscopy indicated that the fabricated powders coincided with hydroxyapatite in nature. In addition, it was found that the BET specific surface area and the adsorption average pore diameter of the nanocrystalline hydroxyapatite powders obtained by this easy microwave assisted synthesis were 94.3 ± 0.6 m^2/g and 18.8 nm, respectively.

Key words: Microwave assisted synthesis, Calcium phosphate, BET specific surface area.

Introduction

Recently, calcium phosphates have not only been considerably focused on as attractive biomaterials but also extensively investigated because of their excellent biocompatibility, potential resorbability, molding capabilities, and easy manipulation [1]. Among them, hydroxyapatite (HAp) is an attractive biomaterial for bone and tooth implants, which has received considerable attention because of its chemical similarity to natural bone and its excellent biocompatibility. Depending upon the technique used for HAp particles preparation, materials with multifarious morphologies, stoichiometry, and crystallinity have been obtained [2].

On the other hand, it is well known that microwave assisted synthesis is a fast, simple and efficient method to prepare organic materials. Compared with conventional methods, microwave assisted synthesis has the advantages of a rapid heating rate, reduced processing times, substantial energy saving, and is environmental-friendly. Microwave assisted synthesis of calcium phosphate has many advantages such as rapid growth, a nano-scaled particle size, and a narrow particle size distribution due to fast homogenous nucleation [3]. Accordingly, some researchers have reported using microwaves to prepare nano-sized calcium phosphates [3-10]. However, there is no report as yet to prepare nanocrystalline HAp by instant microwave assisted synthesis with calcium hydroxide ($Ca(OH)_2$) and phosphoric acid (H_3PO_4).

In this study, we prepared nanocrystalline HAp to fully utilize the microwave assisted synthesis. In order to inhibit the creation of by-products, $Ca(OH)_2$ and H_3PO_4 were used as below. By thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and BET analysis, the properties of the as-prepared nanocrystalline HAp powders were investigated.

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O \quad (1)$$

Experimental Details

0.3 M of H_3PO_4 was poured into a beaker containing 0.5 M of $Ca(OH)_2$ and 1,000 ml of distilled water. Immediately, the mixture was subjected to a commercial microwave oven (Whirlpool household microwave oven AVM541/WP/WH) at 800 W (2.45 GHz) for one hour. The beaker was carefully taken out from the microwave oven and then the precipitate was centrifuged at 6,000 rpm for 30 minutes by a MIKRO 22R (Hettich, Germany). The supernatant liquid was poured out and the product put in a dry oven to evaporate the residual water at 60 °C for 24 hours. Finally, the powder was obtained by grinding with an agate mortar and pestle.

TGA analysis was performed by a TGA Q 500, TA Instrument. Wide-angle X-ray diffraction (WAXD) measurements of the prepared powder was preformed using an X-ray diffractometer (Rigaku Denki D-Max2000, Rigaku, Tokyo, Japan) operated at 40 kV and 100 mA. The X-ray source was an 18 kW rotating anode X-ray generator equipped with a rotating anode Cu target. The X-ray diffraction patterns of the prepared powder were recorded at room temperature over the range $2\theta = 5 - 60^\circ$ at a scan speed of 5° $minute^{-1}$. To confirm the stoichiometry of the

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obtained powder, EDS analysis (Voyager2, Noran) was used. The particle size and morphology were analyzed in a TEM operated at 80 keV (H-7600S, HITACHI, Japan). TEM specimens were prepared by depositing a few drops of HAp dispersed in distilled water on a carbon coated copper grid. The specific surface area of the powders was determined by the Brunauer-Emmett-Teller (BET) method using a ASAP 2010, Micromeritics Instrument. The powder samples were degassed at 300 °C for 2 h prior to analyses.

Results and Discussion

Fig. 1 shows the TGA curve of the powder obtained. Mass losses in TGA plot represented thermal stability, chemical decomposition or vaporization, and sublimation of the sample at higher temperatures. As seen in Fig. 1, the mass loss of the prepared powder was around 4.3% supporting the fact that there was no phase transformation taking place upon heating. This result clearly indicates that the prepared powder has excellent thermal stability even at high temperature. Furthermore, the change of mass could be attributed to the partial removal of physically absorbed water and possibly lattice water. Therefore, by directly putting the mixture of $Ca(OH)_2$ and H_3PO_4 in the commercial microwave oven, it could be inferred that some inorganic compounds with excellent thermal stability were well prepared.

On the whole, WAXD analysis was used to demonstrate the crystal structure of the products. Fig. 2 shows that the diffraction peaks of the inorganic compound prepared by microwave assisted synthesis are almost similar to those from a conventional wet chemical method. In agreement with the characteristic diffraction peaks of HAp (JCPDS 9-432), it can be conjectured that the inorganic compound from microwave assisted synthesis is HAp. In addition, it can be seen that the diffraction peaks of HAp prepared by microwave assisted synthesis are higher and narrower than those from the conventional wet chemical process

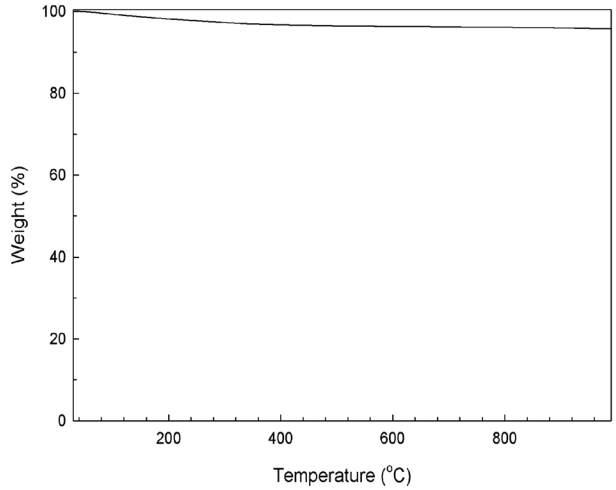

Fig. 1. TGA curve of the prepared powder.

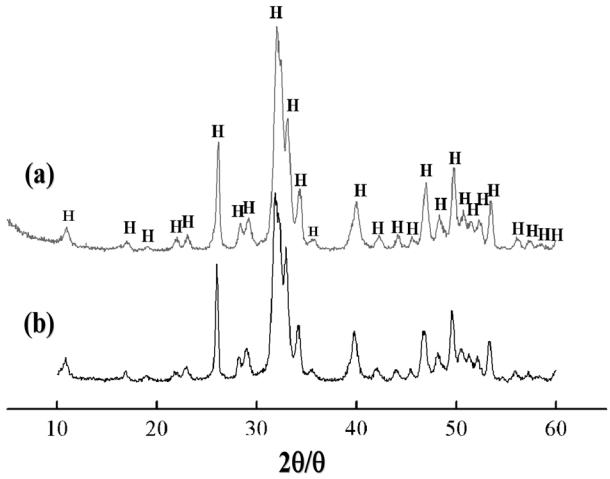

Fig. 2. WAXD data of the powders prepared by microwave assisted synthesis (a) and a conventional wet chemical process (b).

supporting the fact that the HAp powder synthesized by this easy process is relatively well developed.

Fig. 3 shows the EDS analysis of the HAp powder prepared by microwave assisted synthesis. It is known that the Ca/P molar ratio is one of the important characteristics of calcium phosphates to be used as biomaterials. From this EDS data, the Ca/P molar ratio of the HAp prepared in this study could be calculated and it was found to be 1.71, compared with 1.67 in theory. The slight increase of the Ca/P molar ratio would be favorable and fits quite well with that of biological apatite, which ranges from 1.50 to 1.85 [4].

Fig. 4 is a TEM image of the HAp fabricated by microwave assisted synthesis. TEM images indicate the fact that the nanocrystalline HAp particles prepared in this study are rod-like shaped 42.3 ± 1.3 nm in length with a diameter of 15.3 ± 0.4 nm (± standard error). The loose aggregation of the nanocrystalline HAp gives rise to an open but stabilized structure. Additionally, it is responsible for preserving the main advantages of nanocrystals such as a large amount of active surface.

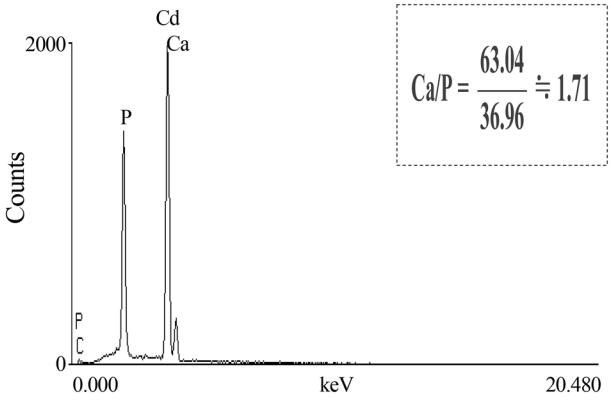

Fig. 3. EDS analysis of the HAp powders prepared by microwave assisted synthesis.

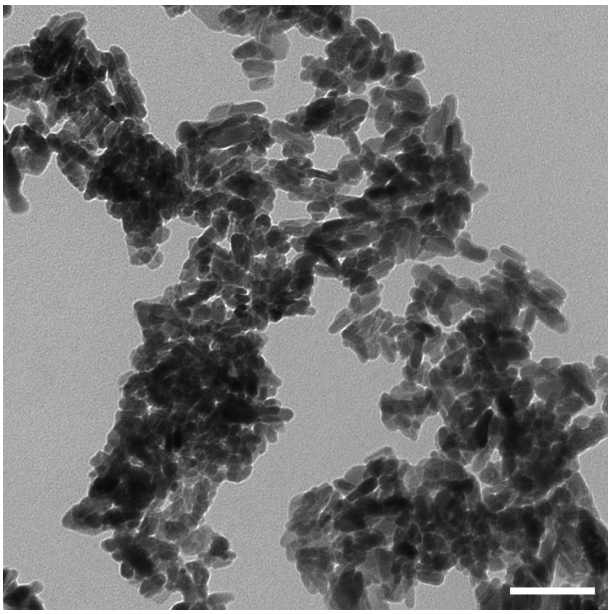

Fig. 4. TEM image of the nanocrystalline HAp powder prepared by microwave assisted synthesis (scale bar : 100 nm).

Fig. 5 shows the nitrogen adsorption isotherm of the HAp powder obtained in this study. The BET specific surface area (S_{BET}) was estimated using adsorption data in a relative pressure range from 0.00 to 0.20. All adsorption isotherms should fit at least one, or at least a combination of two or more, of the six recognized types classified by the Brunauer, Deming, Deming and Teller (BDDT system) [11]. This nitrogen adsorption isotherm of the HAp powder prepared by microwave synthesis shows a typical hysteresis loop indicating that it is type IV in the BDDT system with the presence of mesoporosity which was classified with a pore width between 2-50 nm by IUPAC. Also, it was found that the S_{BET} and the adsorption average pore diameter of the HAp powders were 94.3 ± 0.6 m^2/g and 18.8 nm, respectively. It seems that this easy process can produce HAp powder with a high specific surface area to be applied as a drug delivery system and some absorbents.

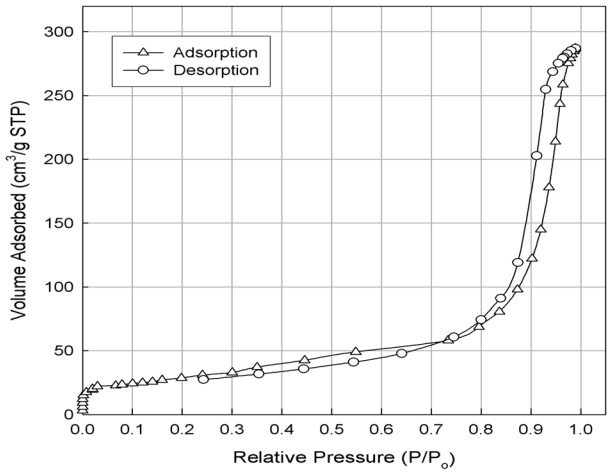

Fig. 5. Nitrogen adsorption isotherm of the nanocrystalline HAp powder prepared by microwave assisted synthesis.

Conclusions

We prepared nanocrystalline hydroxyapatite (HAp) with an easy process. Immediately phosphoric acid and calcium hydroxide were mixed in 1,000 ml of distilled water, the mixture was subjected to a commercial microwave oven adjusted at 800 W (2.45 GHz) for one hour without any delay followed by centrifuging and grinding. By the consequences of investigations including thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), energy dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM), it has been revealed that nanocrystalline HAp powder is well fabricated by microwave assisted synthesis. Furthermore, the result of BET analysis implies that the prepared nanocrystalline HAp powder has mesoporosity and a high BET specific area. In conclusion, it has been shown that this instant microwave assisted synthesis is a suitable and easy process to obtain nanocrystalline HAp powder and they can be used in multifarious medical fields since there are no by-products which cause side effects.

References

1. S.R. Leadley, M.C. Davies, C.C. Ribeiro, M.A. Barbosa, A.J. Paul and J.F. Watts, Biomaterials, 18[4] (1997) 311-316.
2. S. Lazić, S. Zec, N. Miljević and S. Milonjiæ, Thermochimica Acta, 374[1] (2001) 13-22.
3. A. Siddharthan, S.K. Seshadri and T.S.S. Kumar, Scripta Materialia, 55[2] (2006) 175-178.
4. R. Murugan and S. Ramakrishina, Acta Biomaterialia, 2[2] (2006) 201-206.
5. J.-K. Han, H.-Y. Song, F. Satio and B.-T. Lee, Materials Chemistry and Physic, 99[2] (2006) 235-239.
6. C.C. Silva, M.P.F. Graça, M.A. Valente, J.C. Góes and A.S.B. Sombra, Journal of Non-crystalline solids, 352 (2006) 3512-3517.
7. X. Wang, H. Fan, Y. Xiao and X. Zhang, Materials Letters, 60[4] (2006) 455-458.
8. P. Parhi, A. Ramanan and A.R. Ray, Materials Letters, 60[2] (2006) 218-221.
9. J. Liu, K. Li, H. Wang, M. Zhu, H. Xu and H. Yan, Nanotechnology, 16 (2005) 82-87.
10. S.Y. Yoon, Y.M. Park, S.S. Park, R. Stevens and H.C. Park, Materials Chemistry and Physic, 91[1] (2006) 48-53.
11. http://www.staff.ncl.ac.uk.